

# ETCH MASK

## FIELD OF THE INVENTION

The present invention relates to an etch mask which is formed on a surface of a material to be etched, and more specifically to an etch mask, particularly a stripe-shaped etch mask or a diffraction grating-shaped etch mask, useful in forming a required pattern on a semiconductor device.

## BACKGROUND OF THE INVENTION

The present invention relates to the formation of an etch mask on a substrate. As one example of such an etch mask, Fig. 1 shows a prior art etch mask 2a having a predetermined pattern and formed on a surface 1a of a precursor device 1. The prior art mask 2a is stripe-shaped, with a plurality of linear, parallel masks 2b each having a predetermined line width and length. The surface of the masked precursor device 1 is then etched according to the mask pattern. The etch mask 2a is then removed, and another semiconductor material, which may include but is not limited to InP, GaAs, AlGaAs, GaP, InGaAs, AlInGaP, InGaP, GaInAsP, GaN, ZnSe, or CdTe, is laminated thereon as required.

A major problem in semiconductor fabrication is the failure of the mask during processing. Specifically, if etch mask 2a separates from the surface 1a of the precursor device 1 by peeling, delaminating or some other process, or tears or is cut, then the semiconductor material positioned below the disturbed mask portion could be exposed to etchant, and the integrity or functioning of the resultant device could be jeopardized.

The separation or breakage of etch mask 2a may occur due to various factors. If an oxide layer is formed on surface 1a prior to masking the surface, then the mask material, such as a photoresist, may not properly bond or attach to the surface. Semiconductor surfaces are typically treated with hydrogen peroxide or other agents to remove oxide layers and prepare the surface prior to masking. Improper photolithography processing is another cause of separation or breakage of an etch mask. Yet another cause of separation is damage to the mask during etching.

These problems with the prior art can be addressed by means of appropriate previous treating of a surface of the precursor device, appropriate photolithography developing, and appropriate control of the etching. Despite these precautions, the separation of etch masks during etching continues to be a problem.

One problem that has been particularly difficult to solve is the separation of the etch mask during etching that results from excessive etching. In particular, isotropic etching of substrate material near the edge of the mask can result in undesirable modifications of the surface morphology and can weaken the bond between mask and substrate. This is illustrated in Fig. 2, which is a cross-sectional view taken along the line II-II in Fig. 1. As shown by the horizontal arrow, etching perpendicular to the surface of precursor device 1 can reduce the contact area between mask 2b and that device. This may result in separation of the semiconductor material positioned just below etch mask 2a in the vicinity 1A, and as a result etch mask 2a can lift away from the precursor device.

Separation of an etch mask may damage the semiconductor device beyond repair for its intended use. Thus for the structure illustrated in Fig. 1, separation of the mask may limit the usefulness of surrounding areas or even the entire device, and further processing may result in a defective product. Detection of potentially defective products is difficult, and usually does not occur until later in the manufacturing process. The delay and additional processing results in an increase in manufacturing costs.

As described above, the separation of etch masks in manufacturing of a semiconductor device has been a serious problem.

Japanese Unexamined Patent Publication No. Hei. 9-232682 discloses one method that addresses the problem of separation. The etching process of that method is performed by the use of a etch mask in which all ends of the adjacent linear mask 2b have been connected and integrated as shown in prior art Fig. 3, or with an etch mask in which a linear mask perpendicular to all linear masks 2b has been provided on each linear mask 2b shown in Fig. 3, as shown in prior art Fig. 4.

However effective these techniques are in the prevention of separation of the etch mask, other problems result from its use. One problem that may occur from the use of an etch mask is a variation in etch rate. At the point where adjacent linear masks are connected to each other, a smooth flow of etchant is suppressed. The resultant variation in etch rate can result in an unacceptable variation of the dimensional accuracy of the device.

Another problem is defectiveness in layer formation when another semiconductor material has been laminated as a layer after etching. For example, in the manufacturing of a light-emitting semiconductor device, when a mesa stripe formed by etching is formed as a current contracted portion, a current blocking layer needs to be grown on the side of this current contracted portion,

that is, an etched portion. However, a desired current blocking layer is difficult to grow in the periphery where adjacent linear masks are connected to each other, that is, an end portion of the mesa stripe.

## SUMMARY OF THE INVENTION

An aspect of the present invention is to provide an etch mask that can prevent separation of the etch mask in the vicinity of an end portion of an etch mask.

To attain the above-mentioned aspect, the present invention provides a etch mask formed on a surface of a material to be etched comprising collected linear masks, where a portion of the linear mask in the vicinity of an end portion of the etch mask or in the vicinity of an end portion of the material to be etched has a wider portion or a zigzag-shaped portion as compared with the remaining portions.

It is one aspect of the present invention to provide an etch mask on a material to be etched comprising an elongated portion, and an end member connected to said elongated portion, where the width of said elongated portion adjacent to said end member is an end width, where said end member has a maximum extent measured in the direction of said end width, and where said maximum extent of said end member is greater than said end width.

It is another aspect of the present invention to provide a mask pattern comprising a plurality of portions on a material to be etched, said plurality of portions including two end portions, and an elongated portion disposed between said two end portions, where in the vicinity of said two end portions, said elongated portion has an end width, said end portion has a maximum extent measured in the direction of said end width, and where said maximum extent is greater than said end width.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a partial top plan view showing one example 2a of a conventional stripe-shaped etch mask;

Fig. 2 is a partial cross-sectional view taken along the line II-II in Fig. 1;

Fig. 3 is a top plan view of an etch mask disclosed in Japanese Unexamined Patent Publication No. Hei. 9-232682;

Fig. 4 is a top plan view of another etch mask disclosed in Japanese Unexamined Patent Publication No. Hei. 9-232682;

Fig. 5 is a partial top plan view showing one example 12a of a stripe-shaped etch mask according to the present invention;

Fig. 6 is a partially enlarged view in the vicinity of an end portion of the etch mask 12a;

Fig. 7 is a schematic diagram showing the etch mask 12a of the present invention with a material to be etched;

Fig. 8 is a partial top plan view showing another example 22a of a stripe-shaped etch mask according to the present invention;

Fig. 9 is a partial top plan view showing another stripe-shaped etch mask 32a according to the present invention;

Fig. 10 is a partial top plan view showing still another stripe-shaped etch mask 32a according to the present invention;

Fig. 11 is a sequence of cross-sectional views showing the procedures of forming a mesa stripe on a surface of a material to be etched using the stripe-shaped etch mask of the present invention;

Fig. 12 is a partially cutaway perspective view showing a laminated structure of a DFB laser device;

Fig. 13 is a sequence of cross-sectional views showing the procedures of forming a diffraction grating of a semiconductor substrate; and

Fig. 14 is a partial top plan view showing an example of a diffraction grating-shaped etch mask according to the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

One example of a etch mask 12a according to the present invention will be described with reference to Figs. 5 and 6, which show a partial top plan view showing an etch mask 12a formed on a surface 1a of a material 1 to be etched.

Reference to the material to be etched in the present invention refers to material having a surface with an etch mask covering at least a portion of the surface. Material to be etched includes for example, a semiconductor material, an insulating material, and a conducting material. Further, the material to be etched includes a precursor device in which various semiconductor materials have been laminated on a substrate.

Etch mask 12a comprises a plurality of linear masks 12b, each having predetermined line widths and lengths and separations, and formed on a surface of the material 1. The pattern of etch

mask 12a shown in the Figures are illustrative, and are not meant to limit the claims of the present invention.

As shown in Figs. 5 and 6, etch mask 12a in the vicinity 1A of an end portion of the material 1 has a wider portion 12c. The area of wider portion 12c selected to provide protection from separation due to undercutting as described in the prior art.

In one embodiment, the width W of wider portion 12c is wider than a line width Ws of another portion of the linear mask 12b, as shown in Fig. 6. Fig. 7 shows the extent of undercutting due to isotropic etching as dashed lines. Even after undercutting of mask 12c, a material 1d remains in contact with the mask. The greater contact area near the end of mask 12c acts to inhibit or prevent separation of the mask from material 1. Accordingly, the separation of the entire wider portion 12c from the surface of the material 1 to be etched does not occur often. To allow such effects to occur, it is preferable that the width W of the wider portion 12c be two times or more as large as the line width Ws of another portion.

The size of wider portion 12c is limited by some practical considerations. When the wider portion 12c is too wide, the spacing between masks 12b increases and the number of the linear masks 12b which can be formed on the surface of material 1 becomes small. Also, the wider portion 12c may suppress the smooth flow of etchant in the vicinity of the wider portion 12c. If crystalline growth is subsequently preformed on material 1 then the width of the mask may affect deposition as well. Thus, for example, for MOCVD, a line 5  $\mu\text{m}$  width Ws and a 100  $\mu\text{m}$  width W disturbs the distribution of deposition precursors to the extent that it is difficult to get a good crystal quality using MOCVD method.

The shape of materials 1 to be etched may include a circular shape, a rectangular shape and the like. Further, the kinds of the materials 1 to be etched may include, but are not limited to, InP based semiconductors, GaAs based semiconductors, and GaP based semiconductors, insulating materials such as sapphire, quartz, diamond, and SiN, and various conducting materials.

When the material 1 to be etched is a laminated structure of semiconductor materials, it may be comprised of a single layer or a plurality of layers. The laminated materials may include, but are not limited to, a III-V group compound semiconductor and/or a II-VI group compound semiconductor such as InP, GaAs, AlGaAs, GaP, InGaAs, AlInGaP, GaInP, GaInAsP, GaN, ZnSe and CdTe.

Additionally, the material of the above-mentioned etch mask 12a may include, but is not limited to, any one of silicon nitride, silicon oxide, silicon oxynitride and photo-sensitive resist is preferable. Any one of these materials can be easily applied to the formation of the etch mask 12a of the present invention, and the reliability thereof is high.

5 Fig. 8 is a partial top plan view showing an example of another etch mask 22a according to the present invention. Etch mask 22a comprises a plurality of collected linear masks 22b and is formed on a surface of the material 1 to be etched. And portions in each linear mask 22b positioned in the vicinity 1A of end portions of the material 1 have wider portions 22c.

10 In addition to wider portions 22c at the ends of mask 22b, as described previously, etch mask 22a has an additional wider portion 22d disposed between the ends of the mask. In the embodiment shown in Fig. 8, wider portion 22d equally divides the linear mask in the longitudinal direction.

15 The positions and number of wider portions 22d are appropriately selected so that the separation of etch mask 22a can be prevented. The formation of such wider portions 22d can enhance the adhesion force between the etch mask 22a and the material 1 to be etched just below the etch mask 22a by increasing the contact area there between even in a case where the line width of each linear mask 22b is small.

20 Fig. 9 is a partial top plan view showing an example 32a of another etch mask embodiment of the present invention. This etch mask 32a has a plurality of linear masks 32b each having zigzag shapes in a top plan view in portions 32c positioned in the vicinity 1A of the end portions of the material 1 to be etched. Specifically, the end 32c of the etch mask 32a is formed such that the mask end having the same width as the line width  $W_s$  of the linear mask 32b is folded zigzag from side to side a plurality of times (the zigzag is shown as being folded three times, as an example, in Fig. 9).

25 The total elongated length of the zigzag portion in the end 32c, that is the length obtained by the addition of lengths of all zigzag portions, is longer than the linear distance ( $L_0$ ) of the linear mask 32b and the end portion of the etch mask 32a. In other words, the contact area between the end 32c and the material 1 to be etched becomes larger than that in a case the associated end is linear-shaped.

30 Etching of etch mask 32a advances from the end portion of the etch mask during the etching process, decreasing the contact area between mask and material to be etched. However, the contact area per unit length in the end 32c is larger than that of a simple linear shape,

providing additional resistance of separation. At the same time, the advance of the separation is stopped at the folded portions in the zigzag portions. As a result, the separation of etch mask 32a is suppressed.

A preferred etch mask 32a shape that is effective in suppressing separation is one with a total elongated length of the zigzag portions 32c that is two or more times the line width  $W_s$  of the linear mask 32b.

As with the previous embodiments, there are some limitations on the size of the end or enlarged portions. If the total elongated length of the zigzag portions is too long, the length of the linear masks 32b that can be formed on the entire surface of the material 1 to be etched becomes too short to be useful. Further, since a smooth flow of etchant in the vicinity of the folded portions is suppressed, which may present processing uniformity problems. As discussed previously, the subsequent deposition may be affected as well, though the zigzag portion 32c tends to have less of an effect on deposition than does the wider portion 12c.

Additional variations on the zigzag mask are possible. Thus, for example, a middle portion of the linear mask may be modified to include a zigzag portion, as shown in Fig. 10.

In addition to the above-mentioned formation of a mesa stripe, the mask of present invention can be used in the preparation of a diffraction grating in a distributed feedback (DFB) laser device, will be described.

A typical mesa stripe width is usually 1  $\mu\text{m}$  to several tens  $\mu\text{m}$  level. However, the period of the diffraction grating formed in the DFB laser device is usually several hundreds of nanometers level, and the line width of one linear mask may be in the range of several tens nanometers to several hundreds nanometers.

The separation phenomenon of the mesa stripe etch mask almost occurs during etching steps after the etch mask has been formed. However, since the line width of the etch mask used in the formation of a diffraction grating is significantly narrow, the adhesion properties between an etch mask and a semiconductor substrate is deteriorated and such problems often occur that the associated etch mask is separated even in the steps of forming the etch mask.

When an etch mask for a diffraction grating is formed, a negative resist is applied to a semiconductor substrate (a material to be etched) and usually subjected to heat treatment, and then a desired pattern of a diffraction grating is patterning-exposed with an electron beam drawing device. After that, the patterning-exposed portion is cross-linking-cured and is subjected

to a developing process by an alkali solution so that non-patterned portions are removed by dissolution to form a diffraction grating-shaped stripe of resist.

Finally, dry etching is conducted, for example, and a diffraction grating having a desired period and a line width is patterned on a semiconductor substrate (a material to be etched).

5 In this series of formation processes, the resist is etched by an alkali solution during the above-mentioned developing, and the dissolution of the resist advances from an end of the resist. Separation of the resist thus proceeds from the end of the resist.

As explained above, an etch mask having a wider portion or a zigzag portion near its end is effective in suppressing separation of the resist and greatly improves the ability to form  
10 diffraction gratings and other devices. In particular, separation is prevented by increasing the width of the wider portion or by lengthening the zigzag portion. However, if the width of the wider portion is too wide, the width becomes larger than a desired period of the diffraction grating. Accordingly, the end portions of the resists (linear masks) become close to each other or connected to each other and proper etching in the later dry etching steps is suppressed and  
15 further, desired crystalline growth is not conducted in the later layer laminating steps. Further, if the length of the zigzag portion is too long, an appropriate diffraction grating cannot be formed. For such reasons, the upper limits are properly determined.

### EXAMPLES

#### Examples 1 to 8 and Comparative Examples 1 and 2

By the use of an etch mask according to the present invention, a mesa stripe was formed as follows. First, as shown in Fig. 11(a), a surface of a material 1 to be etched having a semiconductor laminate structure containing an active layer was sufficiently subjected to a pretreatment. Typical pretreatment includes an acid bath, followed by a rinse and drying with  
25 nitrogen gas. Acid baths can include one or more of phosphoric acid, hydrochloric acid, and sulfuric acid. Then a 100 nm thick  $\text{SiN}_x$  film 2 was formed by a plasma CVD process.

After pretreatment, a known photoresist was applied onto the  $\text{SiN}_x$  film 2 to form a 1.5  $\mu\text{m}$  thick resist film 3 (Fig. 11(b)). Then, by applying a known photolithography technique to the resist film 3, resist masks 3a corresponding to the etch mask 12a or 22a shown Fig. 5 or 8  
30 respectively in the top plan view were patterned (Fig. 11(c)). Subsequently, as shown in Fig. 11(d), an  $\text{SiN}_x$  film 2 positioned at a portion other than just below the resist mask 3a was etched by an RIE (Reactive Ion Etching) process and the entire resist mask 3a was removed whereby



various stripe-shaped mask bodies 12a (22a) shown in Table 1 were formed on the surface 1a of the material 1 to be etched (Fig. 11(e)).

Then, the resultant structure was transferred to an etching step and exposed material portions, which were not covered with stripe-shaped mask bodies 12a (22a), were etched to form  
5 mesa stripes (current contracted portions) on the surface of a substrate (Fig. 11(f)).

The state of separation in the stripe-shaped mask bodies 12a (22a) was inspected immediately after the etching step. The inspection results are shown in Table 1 together with the size factors of the linear masks.

As apparent from Table 1, the separation or peeling of the etch mask is significantly  
10 reduced or does not occur at all for stripe-shaped mask bodies 12a (22a) having wider portions. Slight separation was found only in a linear mask having no wider portion in its middle portion. As explained above, the usefulness of forming a wider portion in the middle portion of the mask is clear.

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TABLE 1

	Size factors of linear masks			Presence or absence of wider portion in the middle portion of linear mask	State (*) of separation just after etching step
	Width of wider portion in the vicinity of end portion (W: $\mu$ m)	Line width of linear mask (Ws: $\mu$ m)	W/Ws		
Comp. example 1	4.5	4.5	1	Absent	10-20% separated
Comp. example 2	3.0	3.0	1	Absent	10-30% separated
Example 1	9.0	4.5	2	Absent	Not separated
Example 2	9.0	4.5	2	Present	Not separated
Example 3	6.0	3.0	2	Absent	Not separated
Example 4	6.0	3.0	2	Present	Not separated
Example 5	6.75	4.5	1.5	Absent	5% or less separated
Example 6	6.75	4.5	1.5	Present	2% or less separated
Example 7	4.5	3.0	1.5	Absent	7% or less separated
Example 8	4.5	3.0	1.5	Present	3% or less separated

(\*) indicated by the percentage of the number of separated mask bodies to the number of mask bodies formed

Examples 9 to 18 and Comparative Examples 3 to 6

To form a DFB laser device shown in Fig. 12, an n-InP buffer layer 42, an MQW-SCH layer 43, and an under portion 44A of a spacer layer of p-InP were sequentially laminated on an n-InP substrate 41, and diffraction gratings were formed on the under portion 44A of the spacer layer as will be described later. Note that a laminated structure from the substrate 41 to the under portion 44A of the spacer layer is referred to as a material 1 to be etched.

As shown in Fig. 13(a), an about 100 nm thick electron beam drawing negative-type resist 4 was applied onto the material 1 to be etched with a spin coater, followed by heat treatment.

Then, by the use of an electron beam drawing device, a diffraction grating pattern was drawn on the negative-type resist 4 as shown in Fig. 13(b). The resultant drawn pattern is shown in Fig. 14. After that a predetermined heat treatment and developing process were performed, and portions of a unexposed resist were removed to expose the surfaces 1a of the material to be etched as shown in Fig. 13(c). Then, dry etching was conducted to pattern a diffraction grating 5 as shown in Fig. 13(d).

The size factors of the resultant diffraction grating 5 are shown in Table 2. Also the state of peeling or separation of a resist (etch mask) just after a developing process is also shown in Table 2.

As apparent from Table 2, separation is reduced more significantly than in Examples 3 to 6, with wider portions having little or no separation. Specifically, when the width ( $W_y$ ) of the wider portion is set to two times or more the line width ( $W_x$ ) of the linear mask, no separation occurs.

Table 2

	Size factors of linear masks				State (*) of separation just after etching step
	Line width of linear mask (Wx:nm)	Width of wider portion in the vicinity of end portion (Wy:nm)	Pitch between diffraction gratings (Wz:nm)	Length of linear mask (Wp: $\mu$ m)	
Comp. example 3	100	100	300	20	About 20% separated
Comp. example 4	50	50	300	20	80% or more separated
Comp. example 5	100	100	500	20	About 20% separated
Comp. example 6	50	50	500	20	80% or more separated
Example 9	100	150	300	20	None
Example 10	100	200	300	20	None
Example 11	50	75	300	20	5% or less separated
Example 12	50	100	300	20	None
Example 13	50	150	300	20	None
Example 14	100	150	500	20	None
Example 15	100	200	500	20	None
Example 16	50	75	500	20	5% or less separated
Example 17	50	100	500	20	None
Example 18	50	150	500	20	None

(\*) indicated by the percentage of the number of separated mask bodies to the number of mask bodies formed

While the above examples describe the use of a dry etching process, wet etching may be used. If the etchant of wet etching does not chemically react on the negative resist, then no SiN<sub>x</sub> underlayer may be required. If the wet etchant chemically reacts with the negative resist, then a SiN<sub>x</sub> underlayer may be required. As an example of processing in this case, the mask is prepared by photolithography. A dry RIE step is then used to etch the SiN<sub>x</sub> layer, followed by wet etching of the patterned substrate.

#### Examples 19 to 26 and Comparative Examples 7 and 8

Various stripe-shaped mask bodies were formed on a material to be etched in the same manner as in Examples 1 to 8, except that the etch mask was the etch mask 32a shown in Fig. 9 and the etch mask shown in Fig. 10. The resultant structure was transferred to an etching step. Then, the exposed portions not covered with the stripe-shaped etch mask were etched to form mesa stripes (current contracted portions) on the surface of a substrate.

The state of peeling or separation in the stripe-shaped mask bodies was inspected just after the etching step. The inspection results are shown in Table 3 together with the size factors of the linear masks.

As apparent from Table 3, the separation of the etch mask was significantly reduced or did not occur at all for stripe-shaped mask bodies having zigzag portions.

Table 3

	Size factors of linear masks			Presence or absence of wider portion in the middle portion of linear mask	State (*) of separation just after etching step
	Line width of linear mask (Ws:µm)	Total elongated length of the zigzag portions (L:µm)	L/Ws		
Comp. example 7	4.5	--	--	Absent	10-20% separated
Comp. example 8	3.0	--	--	Absent	10-30% separated
Example 19	3.0	6.0	2	Absent	2% or less separated
Example 20	3.0	6.0	2	Present	Not separated
Example 21	3.0	15.0	5	Absent	Not separated
Example 22	3.0	15.0	5	Present	Not separated
Example 23	4.5	9.0	2	Absent	2% or less separated
Example 24	4.5	9.0	2	Present	Not separated
Example 25	4.5	22.5	5	Absent	Not separated
Example 26	4.5	22.5	5	Present	Not separated

(\*) indicated by the percentage of the number of separated mask bodies to the number of mask bodies formed

After the etching process, all mask bodies were transferred to a cleaning step and the state of separation in the mask bodies just after the cleaning step was inspected. Slight separation was observed only in a linear mask having no wider portion at the middle portion. Based on the fact, as explained above, the usefulness of forming a zigzag portion in the middle portion of the mask is clear. As described above, according to the etch mask of the present invention, by forming a wider portion or a zigzag portion in a linear mask positioned in the vicinity of an end portion of a material to be etched, or if necessary by forming a wider portion or a zigzag portion in at least one portion other than the portion in the vicinity of the end portion, the separation of the etch mask in an etching step and the following cleaning step can be prevented, and at the same time, the occurrence of etching variations in the etching step and the layer defects in the layer laminating step after the etching step can be prevented.

By the above-described effects, the yield in manufacturing the semiconductor device can be enhanced and the cost reduction (working man-hour, costs in members and the inspection costs) can be realized. Further, an array-structured device comprised of a plurality of mesa stripes and a diffraction grating-built in DFB laser device can be also stably manufactured.